

Electrophoresis and Electrical Conductivity of Suspensions under the Conditions of Quasi-Equilibrium Polarization of the Double Layer as a Whole

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Abstract – The double layer as a whole includes a diffuse part and other structural parts such as, for example, the Stern layer (a porous adsorption layer). Phenomenologically, polarization and, consequently, the electrokinetic behavior of a particle are described by a set of parameters (phenomenological invariants); the moments of double layer and partial surface conductivities for each type of ion should be used as such parameters. On a molecular level, the task is to express these phenomenological invariants in terms of parameters characteristic of individual parts of the double layer. Calculations were performed for a model of a thin adsorption layer, for which the Henry–Stern isotherm is valid. The conductivity increment for such a system was shown to be very sensitive to the mobility of adsorbed potential-determining ions. The magnitude of this mobility may be evaluated by measuring adsorption and conductivity in a wide concentration range

The aim of this paper is to combine various approaches to considering the polarization of constituent parts of the electrical double layer. The basic assumptions underlying this study are quasi-equilibrium polarization (i.e., for ionic concentration in some volume, the relaxation time is of the same order of magnitude as the time of diffusion relaxation) and the thickness of the electrical double layer (the thickness of the diffuse part amounts to a predominant fraction of the overall thickness) is small as compared to particle size.

TWO LEVELS IN DESCRIBING THE SURFACE OF A PARTICLE

The theory of electrokinetic phenomena uses two principal approaches [1]. The first one – the phenomenological approach – establishes the relationship between the magnitude of observed phenomenon and a set of certain phenomenological parameters describing the surface. The extent of the correlation between a certain set of parameters (phenomenological invariants) and a specific set of experimental data offers a criterion to assess the validity of this approach. It is an advantage of this approach that phenomenological invariants are derived directly from the experimental results and are as reliable as direct observations. The weaknesses of this approach are a continuation of its merits: by operating with phenomenological invariants only, it is impossible to make any specific conclusions about why the values of the discussed invariants are these, and not

any other values. Phenomenological theory quite solidly considers the problem “how”, but is almost helpless in explaining “why.”

The other approach, which is traditionally denoted as a model approach (we believe that it is more appropriate to speak of a molecular level or approach), rests on assuming a certain microscopic (molecular) model. On the basis of this model, both phenomenological invariants and the actual observed effects can be calculated. The approach may be considered fruitful when it involves a minimal number of parameters, which have clear physical meaning, and the predictions allowed by this approach are meaningful. The major advantage of this approach is the clarity of elementary physical processes underlying the phenomenon. The principal drawback is that it requires an *a priori* model.

The drawbacks of both approaches may be compensated by using them together, that is, by combining them. In this case, experimental data are interpreted in terms of theory of the first level (i.e., in terms of phenomenological invariants), whereas the molecular theory is used to analyze microscopic processes and properties that bestow a specific value to the invariant.

In this study we strive to demonstrate the advantages of the combined method by way of an example involving the analysis of the contributions of polarizations of diffuse and compact parts of the electrical double layer to conductivity during electrophoresis.

BASIC SET OF EQUATIONS

Consider an electrolyte of arbitrary composition, which contains ions of N types with valences z_i ($z > 0$ for cations and $z < 0$ for anions), and diffusion coefficients D_i at concentrations C_i . Within the framework of the ionophoretic approach [2, 3], the equations for the flux rate of liquid \mathbf{v} , flux pressure p_1 , and flux chemical potentials μ_i (these are dimensionless quantities reduced to RT) are as follows

$$\begin{aligned} \eta \operatorname{rot} \operatorname{rot} \mathbf{v} + \nabla p_1 + RT \sum_{i=1}^N C_i \gamma_i \nabla \mu_i &= 0, \\ \operatorname{div} \mathbf{v} &= 0, \\ \operatorname{div} [(1 + \gamma_i) (-D_i \nabla \mu_i + \mathbf{v})] &= 0, \end{aligned} \quad (1)$$

where η is the viscosity of liquid, and $\gamma_i(\mathbf{r})$ is equilibrium local excess concentrations of the ions of i th type with respect to bulk concentration (γ_i is also a dimensionless quantity reduced to C_i).

The approach using chemical potentials of individual ions is rather popular [4, 5], especially in the studies of systems containing ions of more than two types. However, formal usage of μ_i variables is not always associated with the true understanding of the physical meaning of the substitution performed, or of the dramatic simplifications introduced by this substitution into the initial set of electrokinetic equations.

The term flux quantity refers to the thermodynamic force causing the associated flux. For example, the electrical double layer is characterized by an equilibrium potential difference and equilibrium electric field; however, they do not cause electric current. Such an electric field is not a flux quantity. Polarization of the double layer by some external action distorts the equilibrium electric field; if this distortion gives rise to electric current, the corresponding component of the potential is a flux electric potential.

In the set of equations of creep flow and convective diffusion (1), it is the local concentration excesses γ_i that are the most physically important quantities. Sticking to phenomenological methodology, we ignore the fact that the concentrations of ions at the surface of particles are different from concentrations in bulk; we assume that this difference does exist and is confined to a relatively thin layer.

The procedure described in [6] makes it possible to express the contribution from a thin surface layer in the form of a boundary condition. Applying this procedure to equations of convective diffusion in (1) reveals that beyond the surface layer, the flux chemical potentials μ_i satisfy the Laplace equation

$$\Delta \mu_i = 0. \quad (2)$$

At the surface of a spherical particle of radius a , the following boundary condition holds true:

$$(-D_i) \frac{\partial \mu_i}{\partial r} \Big|_{r=a} = \frac{1}{a \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta J_{si}), \quad (3)$$

$$J_{si} = -\Gamma_{0i} \frac{\partial \mu_i}{a \partial \theta} + W_i, \quad (4)$$

$$\Gamma_{0i} = \int_0^\infty D_i(x) \gamma_i(x) dx, \quad (5)$$

where J_{si} is the surface flux of the ions of i th type; Γ_{0i} is the weighed total excess of the ions of i th type in the surface layer. These calculations are described in detail in [7]; the structure and meaning of electroosmotic correction factors W_i are also discussed there. These factors are significant for counterions and are always small for co-ions. As demonstrated in [8], under certain conditions, these factors may be included into Γ_{0i} as additional components. In this study, we ignore these factors.

In writing expression (5) for the total excess, we assume that the diffusion coefficient may be a function of the distance to the surface (in the simplest case this dependence may be stepwise, with the steps associated with the boundaries between structural parts of the double layer). However, if one assumes that the diffusion coefficient is constant within the surface layer, the total excess is equal to the product of diffusion coefficient by dimensionless adsorption of the ions of the i th type.

To solve the equation of creep flow, let us make use of the fact that the surface layer is thin and may be considered locally planar. The liquid outside the limits of the surface layer satisfies Stokes' equations

$$\begin{aligned} \eta \operatorname{rot} \operatorname{rot} \mathbf{v} + \nabla p_i &= 0, \\ \operatorname{div} \mathbf{v} &= 0. \end{aligned} \quad (6)$$

The effect of surface layer is reflected in the boundary conditions on the surface of a particle:

$$\begin{aligned} v_x|_{x=0} &= 0, \\ v_y|_{x=0} &= -\frac{RT}{\eta} \sum_{i=1}^N C_i \Gamma_{1i} \frac{\partial \mu_i}{\partial y} \Big|_{x=0}, \end{aligned} \quad (7)$$

$$\Gamma_{1i} = \int_0^\infty x \gamma_i(x) dx \quad (8)$$

(the details are described in [7]). The magnitude of Γ_{1i} given by formula (8) is the first moment of local concentration excess (adsorption is the zero moment). In this formula, the lower integration limit coincides with the position of the slipping plane, so that the integration is performed over only the mobile part of the surface layer.

Hence, we demonstrated that electrokinetic behavior of a particle with a thin surface layer is described by equations (2) and (6) for the bulk solution that must be solved with boundary conditions (3) and (7). The effect of the surface layer on electrokinetic phenomena is mediated via the quantities Γ_{0i} and Γ_{1i} , which are the above described phenomenological invariants of the theory.

ELECTRICAL CONDUCTIVITY AND PHENOMENOLOGICAL INVARIANTS

To calculate electrical conductivity, let us first calculate the distribution of flux chemical potential μ_i around a spherical particle placed into a homogeneous flux of ions of the i th type (such a flux corresponds to the μ_i gradient that is uniform over a large distance from the particle). Solution of the Laplace equation (2) satisfying the condition

$$\nabla \mu_i|_{r \rightarrow \infty} = A_i \quad (9)$$

and condition (3) is

$$\mu_i = \cos \theta (A_i r + B_i / r^2), \quad (10)$$

where B_i is the induced dipole moment of a particle, which is given as

$$B_i = \frac{a^3 A_i}{2} \frac{1 - 2R_i}{1 + R_i}. \quad (11)$$

Formula (11) involves partial polarization criterion Rel_i (R_i in abbreviated form)

$$R_i = \Gamma_{0i} / (D_i a), \quad (12)$$

which actually represents the appropriately reduced total excess. The physical meaning of R_i is the dimensionless partial surface conductivity of a particle with respect to the ions of the i th type.

Variation of the flux Δj_i of the ions of the i th type is associated with the presence of disperse particles, whose content in solution is characterized by a small volume fraction α . According to [6], this variation is unequivocally related to the induced dipole moment as

$$\Delta j_i = (-3B_i C_i D_i \alpha) / a^3. \quad (13)$$

If a uniform gradient of chemical potential μ_i is caused by external electric field E ,

$$A_i = -z_i F E / (RT), \quad (14)$$

and the variation of electric current ΔI associated with polarization of particles is given as

$$\Delta I = \sum_{i=1}^N z_i F \Delta j_i = -\frac{3}{2} K \alpha E \sum_{i=1}^N t_i \frac{(1 - 2R_i)}{(1 + R_i)}, \quad (15)$$

where t_i is the transport number for the ions of i th type in solution,

$$t_i = z_i^2 D_i C_i / \sum_{i=1}^N z_i^2 D_i C_i,$$

and

$$K = \frac{F^2}{RT} \sum_{i=1}^N z_i^2 D_i C_i \text{ are the conductivity of solution.}$$

Thus, the increment to conductivity associated with the disperse particles is described as

$$\text{Inc} = (\Delta I) / (K \alpha E) = -\frac{3}{2} \sum_{i=1}^N t_i \frac{1 - 2R_i}{1 + R_i}. \quad (16)$$

Expression (16) is identical to the equation reported by O'Brien [4] for the conductivity of dilute suspensions in an electrolyte of arbitrary composition. This is not surprising, because all phenomenological theories that rely on the same initial equations produce identical results. Differences arise on a molecular level.

Thus, we established that the low-frequency limit for the conductivity of a suspension is expressed in terms of R_i , which is the phenomenological invariant of this effect.

ELECTROPHORESIS AND PHENOMENOLOGICAL INVARIANTS

To calculate the rate of electrophoresis, let us make use of the well-known result [9] relating the velocity of electrophoresis of a sphere to the velocity of electroosmotic slippage at the equator of this particle:

$$V_{\text{eph}} = -\frac{2}{3} V_{eo} \Big|_{r=a, \theta=\pi/2} \quad (17)$$

The slippage velocity at the equator is given by the combination of equations (7), (10), and (14). Finally,

$$V_{\text{eph}} = -\frac{FE}{\eta} \sum_{i=1}^N z_i C_i \Gamma_{1i} / (1 + R_i). \quad (18)$$

This formula demonstrates that partial polarization criteria and moments of the surface layer, which were both discussed above, are the phenomenological invariants for the description of electrophoresis.

THE ELECTRICAL DOUBLE LAYER AS A WHOLE AND ITS CONSTITUENT PARTS

After discussing briefly the phenomenological theory, we proceed by analyzing a molecular model that allows the calculation of the required invariants.

The following models are usually considered.

(a) A standard electrokinetic model, in which a fixed charge lies on a mathematical plane identified with the surface of a particle; this charge is assumed to be immobile, whereas the charge of the diffuse part of the double layer is mobile.

(b) The Dukhin–Seminikhin model [10], which is different from the preceding model in that the internal part (adjacent to the surface of a particle) of the diffuse layer is assumed to be hydrodynamically immobile.

(c) A model of mobile ions of the Stern layer, which supplements the standard model by assuming that the ions adsorbed at the surface may have a finite mobility. This model was qualitatively discussed in [11, 12]. Simonova and Shilov [13] used this model to elaborate a quantitative theory of electrophoresis and conductivity.

(d) A model of a porous surface layer in which, in contrast to the preceding model, the adsorbed ions are assumed to stay within a layer of finite thickness [14, 15] rather than on an infinitely thin plane.

(e) A united model may be considered that combines all characteristic structural elements of the preceding models: a porous adsorbed layer of finite thickness, a hydrodynamically immobile part of the diffuse layer, and a conventional diffuse layer.

Figure 1 compares these models.

Let us examine whether it is justified to assign the Stern layer a finite thickness [models (d, e)] instead of identifying it with the thickness of a monolayer [model (c)]. The Stern isotherm of adsorption was suggested in electrochemistry to explain the patterns of electrocapillary curves. The following specific features are inherent to the corresponding experiments: the surface (of mercury) is smooth on a molecular level, that is, it has the least roughness available in nature; the surface possesses the highest possible energetic uniformity; the concentration of electrolyte is high (moles per liter) and the diffuse double layer is very thin (almost completely suppressed).

The combined effect of these three features makes it possible to reveal the role of the structures with dimensions on a molecular scale, that is, the role of the adsorbed monolayer identified, as conceived, with the Stern layer on the surface of mercury.

When these concepts (which are quite universal from a physical point of view) are applied to colloidal objects, the specific features of these objects are often ignored: a molecularly smooth surface for them is an exception (e.g., mica) rather than a rule; energetic uniformity of any solid surface (especially crystalline) is very rare, nonuniformity associated, for example, with the presence of adsorption sites being a rule; the upper limit of electrolyte concentrations lies in a centimolar, rarely decimolar, range, which corresponds to the thickness of diffuse layer of the order of magnitude of 10 Å.

When these three specific features act together, the role of the structures with molecular dimensions is

strongly disguised, because both the roughness of the surface and the diffuse layer are the structures with supermolecular dimensions. This is why, we believe, the concept of a porous surface layer, otherwise, the Stern layer of finite thickness, makes it possible to reflect the specific features of the surface structure of colloidal particles without getting involved in detailed geometrical modeling (i.e., without involving the concepts of fractal surfaces).

BINARY ELECTROLYTE

Let us specify general formulas for a particular case of a 1 : 1 binary electrolyte. The situation is the simplest with the moments of double layer, because only the diffuse periphery of the double layer contributes to these:

$$\Gamma_1^+ = 4 \ln((1 + \exp(\mp \zeta/2)) / 2) / (\kappa a)^2, \quad (19)$$

where ζ is the potential of the slipping plane and κ is the reciprocal radius of shielding in solution (see [7] for details).

For partial surface conductivities, integral (5) gives a sum over individual parts of the double layer. Denoting the potential of the boundary of the diffuse layer [which does not coincide with ζ -potential for models (c) and (d)] by ψ_δ , we come to the following formula for conductance of the diffuse layer (the so-called Bikerman's surface conductance) [16]:

$$R^\pm = (\exp(\mp \psi_\delta/2) - 1) / (\kappa a). \quad (20)$$

We call surface conductance over other structural parts of the double layer additional surface conductance. The corresponding calculations are described in [17] for model (c) and in [18] for model (d).

ζ -POTENTIAL AND PHENOMENOLOGICAL INVARIANTS

Is ζ -potential a phenomenological invariant? By substituting expressions (19) for the moments into electrophoretic formula (18), one may easily show that the knowledge of ζ -potential, which is equal to

$$\zeta = -(\kappa a)^2 (\Gamma_1^+ - \Gamma_1^-) / 2$$

makes it possible to predict the velocity of electrophoresis only when all partial surface conductivities are

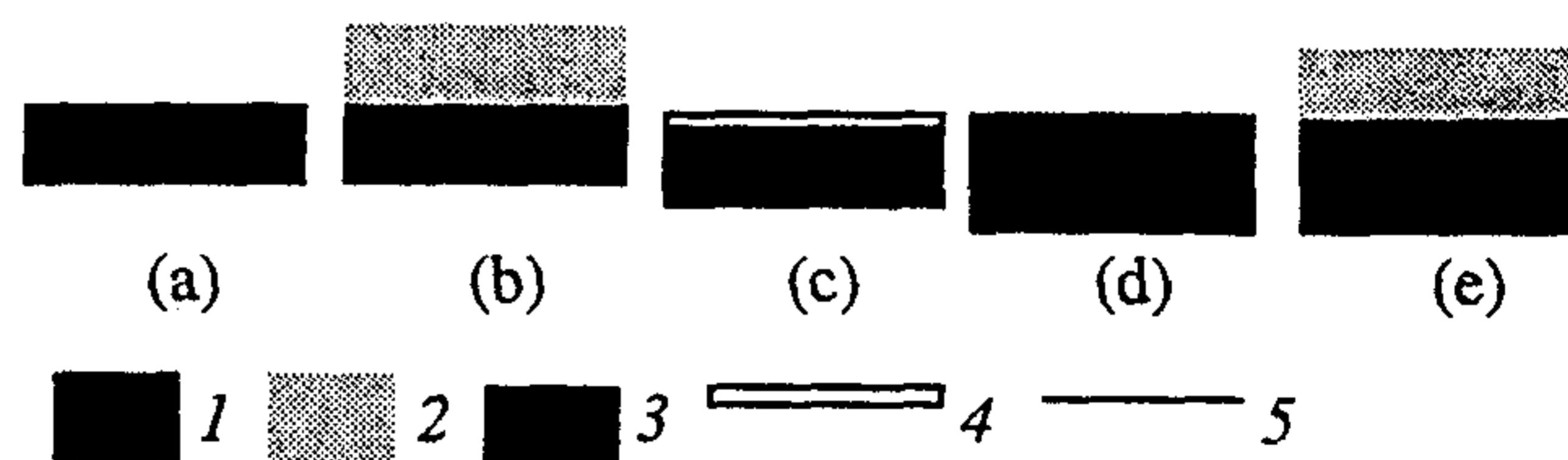


Fig. 1. Different models for the structure of the electrical double layer as a whole. (1) The volume of dielectric impermeable to ions, (2) hydrodynamically immobile layer, (3) porous adsorption layer, (4) schematic depiction of a very thin adsorption layer (Stern layer), (5) outer boundary of the diffuse plate. See the text for discussion.

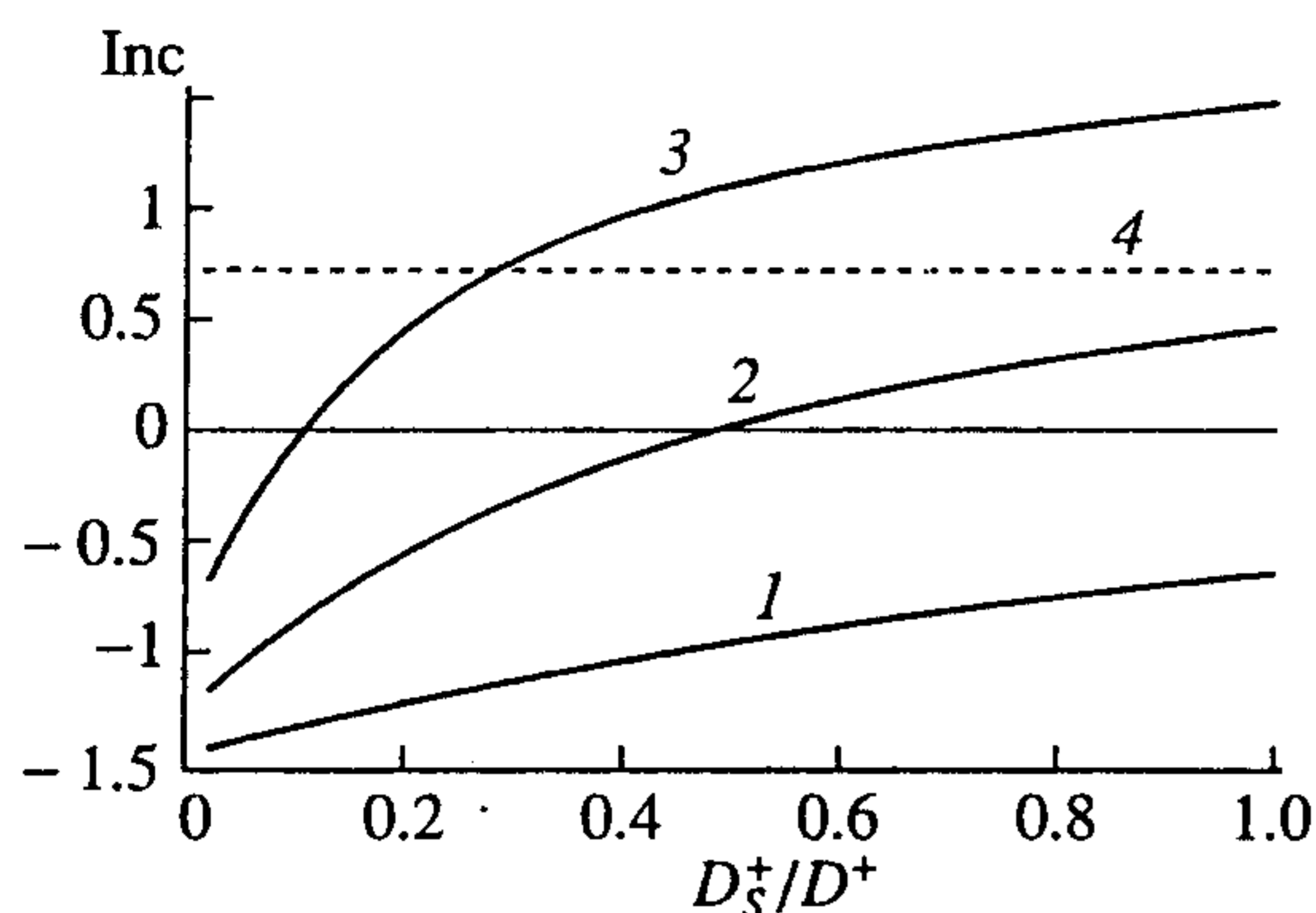


Fig. 2. Conductivity increment as a function of the ratio between diffusion coefficients of potential-determining ions (cations) in the adsorption layer D_s^+ and in bulk solution D^+ . (1) $G^+ = 1000$, (2) 10000, and (3) 100000; (4) shows the upper limit of the increment for unipolar surface conductivity.

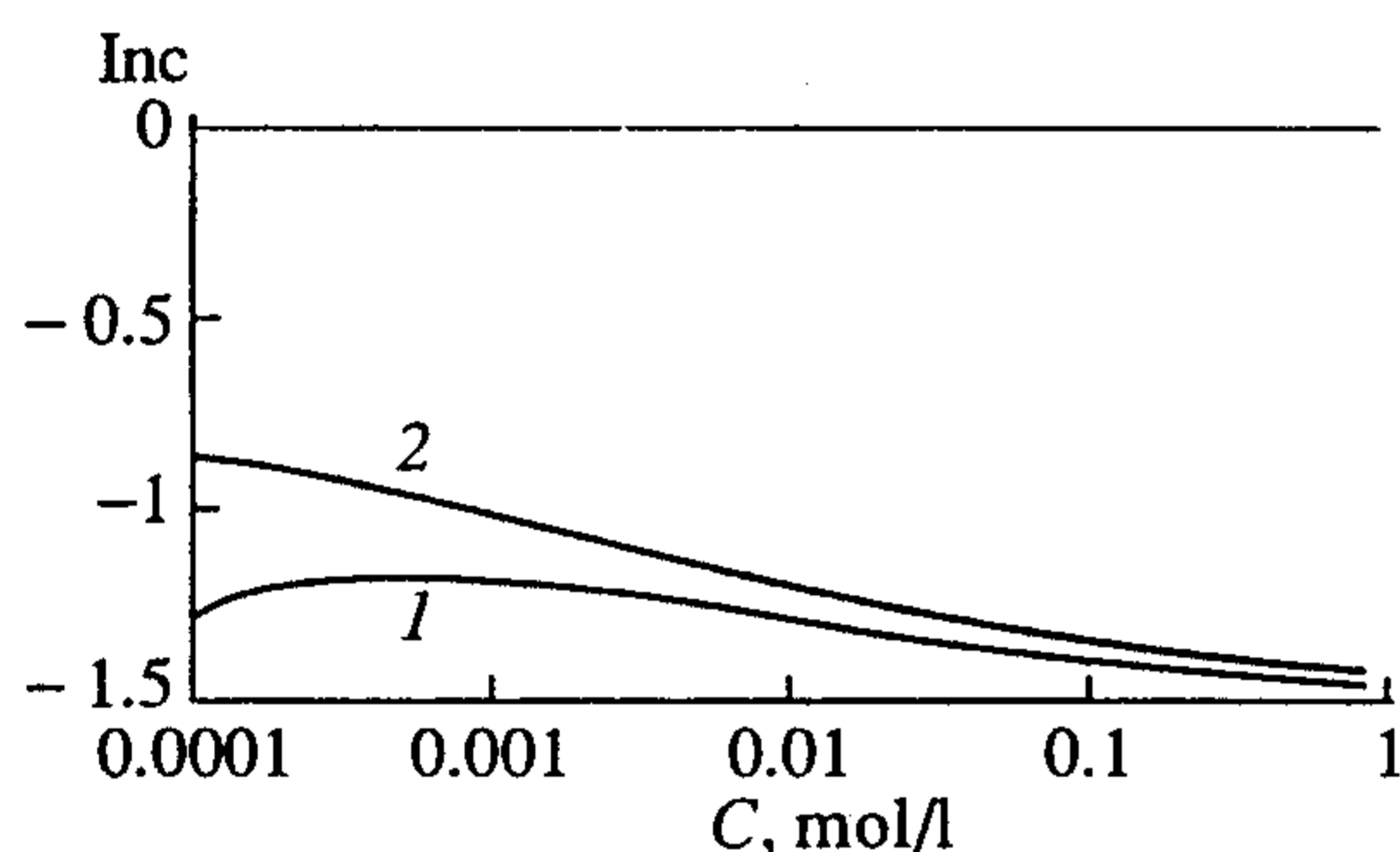


Fig. 3. Conductivity increment as a function of electrolyte concentration C : (1) $D_s^+/D^+ = 0$, (2) $D_s^+/D^+ = 0.1$.

small. When this condition holds true, ζ -potential is a phenomenological invariant. As is common in the development of physical theory, a more general approach does not eliminate one suggested earlier, but specifies the range of its applicability.

If a more complex structural model of the double layer is considered, the ζ -potential is no longer a phenomenological invariant, even in the absence of notable surface conductivities. In the Dukhin–Seminikhin model, the region in which the liquid is hydrodynamically immobile (region 2 in Fig. 1) is assumed to be completely impermeable to the liquid. However, in more complex studies [14, 15, 19], which predominantly elaborate on modeling the electrokinetic behavior of the adsorption layers of polymers, the flow of liquid within the layer is allowed. As demonstrated in [15], in some cases, the contribution of this flow may be taken into account simply by modifying formulas (19) for the moments.

THIN POROUS LAYER

Let us consider in more detail the partial surface conductivities in model (c) (Fig. 1). The basic assumption of this model is that the adsorption of ions occurs in such a thin layer that the variation of potential across this layer may be ignored. In [17], where additional surface conductivity within the framework of this model was studied in detail, this property was called the isopotentiality of the adsorption layer.

The principal inferences made in [17] are as follows. Let the adsorption of ions be described by the Henry–Stern equation

$$M_i = G_i C_i \exp(-z_i \zeta),$$

where M_i is the concentration of adsorbed ions and G_i is the Henry constant. For the adsorbed layer of thickness H , the potential ζ is given by the equation

$$\sinh(\Psi_D - \zeta) = v \sinh \zeta / 2; \quad v = 2 / (\kappa H (G^+ G^-)^{1/2}),$$

where $\Psi_D = 0.5 \ln(G^+ / G^-)$ is the Donnan potential. Using these equations one may write

$$R^\pm = (\exp(\mp \zeta / 2) - 1) / (\kappa a) + (H/a) (D_{is} / D_i) G_i \exp(-z_i \zeta), \quad (21)$$

where D_{is} is the diffusion coefficient within the adsorbed layer and D_i is the diffusion coefficient in bulk solution. The first term in (21) reflects the contribution of the diffuse part of double layer (Bikerman's surface conductivity), whereas the second term corresponds to additional surface conductivity associated with the mobility of adsorbed ions.

Substitute (21) into formula (16) for the conductivity increment and analyze the result for the following set of parameters: $H = 1 \text{ \AA}$; $D^+ = D^-$; $G^+ = 10000$; $G^- = 1$.

Figure 2 illustrates the variation of the increment as a function of the ratio $D_s^+ : D^+$ between diffusion coefficients of potential-determining ions (cations, in the case considered). The increment increases with an increase in adsorption affinity of the cations (concomitantly, the Donnan potential and ζ -potential also grow); it is also quite sensitive to the variation of mobility of potential-determining ions within the adsorption layer. When this mobility increases, the increment also increases, because the unipolar character of surface conductance ensured by the counterions of the diffuse layer is deteriorated. It was reported [6] that at any arbitrarily high unipolar surface conductance, the low-frequency increment of conductivity cannot exceed the limiting magnitude, which is equal to 0.75 (horizontal line 4 in Fig. 2). The flux of adsorbed co-ions reduces the concentration polarization of a particle and the polarization pattern acquires the features characteristic of high-frequency limit, for which the maximum increment is 3.

When the mobility of mobile counterions is taken into account, the magnitude of the increment is affected only slightly (the variation amounts to hundredths of

a fraction, which is indistinguishable on the scale of Fig. 2).

Figure 3 shows the variation of the increment with electrolyte concentration. As can be seen, when there is no flux of the adsorbed co-ions (curve 1), the increment first slightly increases because of the increased charge of the double layer (one should keep in mind that it is the concentration of potential-determining ions that is plotted on the abscissa). When the concentration is increased further, the increment decreases because of the increasing conductivity of bulk solution. The mobility of adsorbed co-ions results in a significantly greater increment, which monotonically decreases as the concentration of electrolyte is increased. In this case, the concentration dependence of the increment is more prominent.

Generally, analysis of the particular case examined here allows a conclusion that the conductivity increment is rather sensitive to the mobility of adsorbed co-ions; the magnitude of this mobility can be determined in complex studies involving the studies of the adsorption of ions and of conductivity in a wide concentration range.

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